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PARTIAL OXIDATION OF PROPANE

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Partial Oxidation of Propane

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Abstract

The oxidation of propane was studied extensively in a flow system at inlet temperatures of 475°C, the temperature region considered most suitable for hydrogen peroxide formation and for which only limited information was previously available. Studies were conducted also at 375°C, thus bracketing the temperature region in which the reaction has a negative temperature coefficient. The major objective was to clarify the reaction mechanism, with particular reference to the rôle of hydrogen peroxide. The results indicate that under the conditions of this work a key reaction is that of the propyl free radical with oxygen which may follow two alternate paths, one forming oxygenated organic products, and the other forming propylene and the perhydroxy free radical. This radical in turn reacts with propane, or another hydrocarbon, to form hydrogen peroxide and a free radical. The negative temperature coefficient of the reaction rate can be explained on the basis of the two alternate

reactions of the propyl radical with oxygen. With an increase in temperature, the reaction which forms propylene was found to increase, relative to that forming oxygenated organics. However, the propylene and perhydroxyl radical formed by the first reaction are known to be less active in continuing chain reactions than the oxygenated organic species alternately formed, thus causing a decrease in the overall rate of reaction.

The above conclusions are of considerable significance in extending the knowledge of the reaction mechanism of hydrocarbon oxidations. The results are also of interest in evaluating the industrial potential of these reactions as methods for manufacture of chemicals.

The oxidation of propane with pure oxygen was studied in a flow reactor under conditions such that appreciable yields of hydrogen peroxide and other intermediate products could be isolated. The objectives of this work were to clarify the reaction mechanism, with particular reference to the role of hydrogen peroxide, and to obtain information which would aid in an evaluation of the industrial potential of the reaction. The experimental conditions covered inlet gas temperatures of 350 to 475°C., propane-oxygen mole ratios of 5.6 to 12.3, and reaction times of 3.2 to 11.8 seconds.

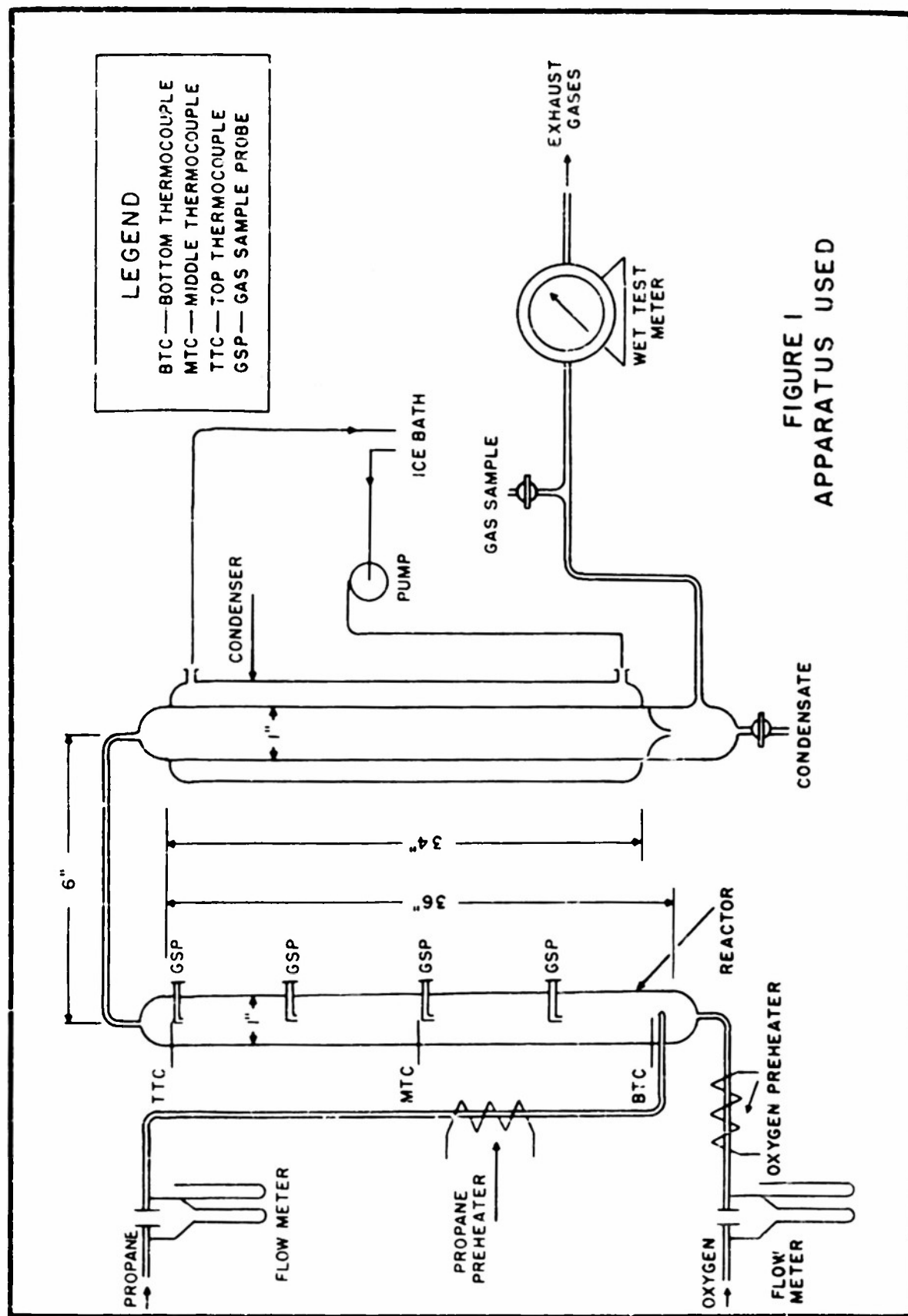
Propane is of particular interest in a study of hydrocarbon oxidation mechanisms, since it is the lowest molecular weight hydrocarbon containing both primary and secondary carbon atoms, and thereby typifies the homologous series of straight chain saturated hydrocarbons. Propane is also readily available from petroleum operations and thus would be a suitable raw material for a possible partial-oxidation process for the production of hydrogen peroxide.

A majority of the previous work reported in the literature on propane oxidation was conducted at temperatures substantially below 400°C and was concerned primarily with the mechanism of the reaction (2), (10), (19), (21), (22), (23). Although considerable speculation existed concerning the exact nature of the reaction, it is now generally believed that at these relatively low temperatures one of the important steps involves

the formation of an alkyl hydroperoxide or an alkyl peroxy radical, which in turn decomposes leading to the formation of aldehydes, methyl alcohol, carbon monoxide, and certain free radicals (17). Propylene, ethylene, hydrogen, methane, and hydrogen peroxide have also been found among the intermediate products under these conditions.

The previous work at temperatures exceeding 400°C. was concerned mainly with the industrial potential of the reaction for production of hydrogen peroxide, and suggested that as the temperature increased the yields of olefins and water increased at the expense of the oxygenated organic products (3), (8), (13), (15). It also appeared that hydrogen peroxide yields were increased at the higher temperature, but the limited information obtained did not permit an interpretation of the reaction mechanism. One of the important objectives of the present work was to obtain a sufficient quantity of accurate, quantitative data under conditions that would permit elucidation of the mechanism of this reaction at temperatures exceeding 375°C.

It was observed by Pease (21) and Kooijman (13) that in a flow system the overall reaction rate has a negative temperature coefficient in the range of 370° to 430°. In the present work quantitative information was obtained at temperatures below and above the range of the negative temperature coefficient, to permit interpretation of this phenomenon.



Experimental Procedure

The equipment consisted of a tubular Pyrex flow reactor, preceeded by separate electrically-heated preheaters for each gas and followed by a tubular surface condenser cooled with water at approximately 0°C. The arrangement of the equipment is shown in Figure 1. The reactor shape was such that the flow characteristics of the gas approximated that of slug flow. Propane of 99% minimum purity and oxygen of 99.5% purity were employed as the reactants. The residence time of the gases within the reactor was varied by changing the inlet gas flow rates. Rapid mixing of the inlet gases was obtained by introducing the propane axially into the oxygen stream through 40 small orifices located on the upper surface of a spiral-shaped glass tube, whose plane was perpendicular to the axis of the reactor.

Temperature control in the reactor itself was obtained by insulating the reactor and winding it with a compensating electrical heater. By adjusting the voltage input, it was possible to maintain essentially isothermal conditions throughout the reactor at low to moderate rates of reaction. At high rates of reaction, such as at 475°C, a substantial temperature increase occurred along the reactor due to the heat of reaction. For this reason, both the inlet and outlet temperatures have been listed in Tables II and III, which give the experimental data and results. During each run the

equipment was allowed to come to a steady state temperature condition before gas and liquid samples were collected. The liquid sample was collected over a measured time interval during which the exhaust gas sample was collected in periodic increments. The exhaust gas flow rate was measured by a wet test meter.

For every run, the gas sample was analyzed volumetrically by chemical absorption for carbon dioxide, propylene, ethylene, oxygen, and carbon monoxide. Hydrogen was determined by passage over heated copper oxide, but it was present in such small quantities that analysis for it was not made in all the runs.

Samples of residual gas from two of the runs (Nos. 65 and 71) were quantitatively analyzed by infra-red absorption*, after removal of oxides of carbon, olefins and oxygen. The instrument had been standardized with mixtures containing known quantities of the following components: methane, ethane, propane, n-butane, iso-butane, neo-pentane, iso-pentane, and 2, 3-dimethyl butane. In both cases, the two components methane and propane accounted for over 98 per cent of the total saturated hydrocarbons. Consequently in a number of other

* This was kindly performed for us by the Research Laboratories Division of the General Motors Corporation.

runs quantitative analysis was made for methane at M.I.T. by use of a Baird Associates infra red spectrophotometer standardized with mixtures of methane and propane after similar removal of the same components. In all runs except numbers 65 and 71, all remaining gas after analysis for specific components is reported in the column headed " C_3H_8 " in the Tables of Results. In all cases this gas consists predominantly of propane but it is seen that it may or may not include small quantities of hydrogen and methane, depending upon whether or not one or both of these species were analyzed for individually. The various procedures for the gas analysis are given by Burke, Starr, and Tuemmler (1).

The condensate from each run was analyzed for total peroxide, total aldehyde, formaldehyde, and methanol. The remainder was assumed to be water. In conjunction with the overall study, various analytical methods for the condensate were evaluated. This evaluation, and the recommended analytical procedure which was used here are presented in detail elsewhere (27). Briefly, the total peroxide was determined iodometrically using 56% hydriodic acid as the reagent and glacial acetic acid as the solvent. Formaldehyde was determined colorimetrically using acidified Schiff's reagent. Acetaldehyde was calculated as the difference between formaldehyde and the total aldehyde, the latter being analyzed by the hydroxylamine method. The methyl alcohol was separated from the condensate by distillation,

after first converting the aldehydes to acid salts with sodium hydroxide-hydrogen peroxide solution, and then determined colorimetrically with ceric nitrate reagent.

Results

In order to determine what saturated hydrocarbons are formed during the reaction, two samples of residual gas were analyzed in detail by infra red absorption as described above, after first removing oxides of carbon, olefins, and oxygen by chemical absorption. The analyses were made on the residual gas from runs 65 and 71, which were conducted at 475°C inlet temperature with a mole ratio of propane to oxygen of 8:1. The results are presented in Table I, together with four tests ^{reported} made on known samples, which compare with actual compositions. The results indicate that methane is the principal saturated hydrocarbon formed, but that minor amounts of ethane are also formed along with traces of n-butane and iso-butane and possibly iso-pentane. The most important result from the standpoint of the reaction mechanism is that 2, 3-dimethyl butane, which would be present if propyl radicals combined with each other, is not formed. The manner in which these saturated hydrocarbons actually found are postulated to be formed is discussed below.

The experimental data, presented in Table II, include for each run the inlet and outlet gas temperatures, the flow rates, and the composition of the exhaust gas from the condenser and that of the condensate. The figures in the column designated

Table I

Paraffin Gas Analysis by Infrared Absorption

Compound	Known I		Known II		Known III		Known IV		Paraffin of Run 65	Paraffin of Run 71
	Actual	Found	Actual	Found	Actual	Found	Actual	Found	%	%
Propane	56.0	58.5	72.8	75.0	88.2	88.7	92.2	91.5	87.0%	78.5%
Methane	20.0	19.0	9.5	9.5	9.8	9.5	4.8	3.8	4.2	10.0
Ethane	4.0	3.5	4.2	4.0	0	3.3	0	0.2	0.5	1.1
n-Butane	4.0	3.2	2.5	1.5	0	0	0	0.1	0.3	0.2
iso-Butane	4.0	4.0	2.5	3.0	0	0	0	0	0.5	0.5
neo-Pentane	4.0	2.7	2.5	2.0	0	0	0	0.6	0	0
iso-Pentane	4.0	3.8	3.5	2.8	3	0.3	0	0.3	0.5	0.7
2,3,-Dimethyl butane	4.0	3.7	2.5	2.8	0	0	0	0	0.1	0
Water	0	0	0	0	2.0	1.5	3.0	3.2	3.0 esti- mated	3.0 esti- mated
Total	100.0	98.4	100.0	100.6	100.0	100.3	100.0	99.7	96.1	94.0

TABLE VI
TABLE OF EXPERIMENTAL DATA

Run No.	TEMPERATURE °C		FLOW RATES		GAS PERCENT (Dry Basis)		EXHAUST		CONDENSATE		COMPOSITION		H ₂ O
	Inlet	Outlet	C ₃ H ₆ O ₂	Exhaust Gas	CO	CO ₂	C ₂ H ₄	C ₂ H ₆	CH ₃ OH	RCHO	CH ₃ CHO	Percent	
67	351 ± 2	340 ± 1	6.83	7.76	0	0	0	0	—	—	—	—	—
68	373 ± 2	340 ± 7	6.19	7.28	0.25	0.3	0.15	0.6	14.4	19.4	17.8	10.9	37.5
69	400 ± 2	402 ± 2	5.94	7.16	0.35	0.2	0.75	0.1	3.7	14.4	19.4	20.4	42.1
69	426 ± 1	427 ± 1	5.76	6.85	0	0.1	0.9	0	—	—	—	—	—
69	450 ± 2	452 ± 1	5.52	6.60	0.1	0	1.75	0.25	1.6	4.0	14.5	20.4	59.5
70a	471 ± 1	600 ± 13	5.33	6.80	4.2	0.3	14.0	10.0	7.2	7.1	1.8	1.2	82.7
80	375 ± 2	390 ± 7	6.19	7.28	0.25	0.3	1.2	0.15	14.4	19.4	17.8	10.9	37.5
80	376 ± 2	419 ± 2	5.63	6.51	1.0	0.25	2.5	0.2	14.4	19.4	12.4	10.6	43.5
91	375 ± 1	419 ± 3	5.06	5.79	0.9	0.27	2.6	0.25	14.4	17.0	14.7	11.8	41.7
92	375 ± 1	415 ± 2	4.38	5.02	1.0	0.25	2.8	0.47	13.7	16.5	14.4	13.1	41.3
93	375 ± 1	417 ± 1	3.60	3.99	1.5	0.1	3.45	0.57	14.4	15.0	14.7	13.9	42.1
96	375 ± 3	300 ± 7	3.61	3.92	2.6	0.4	4.05	0.63	22.4	15.5	14.6	10.8	36.7
97	375 ± 5	303 ± 10	3.61	3.83	3.0	0.5	4.35	0.86	22.2	16.0	13.4	11.5	36.9
98	376 ± 2	379 ± 5	3.11	3.25	4.2	0.5	5.4	0.7	21.0	16.3	9.5	11.7	41.3
98	375 ± 2	379 ± 9	2.52	2.60	5.0	0.6	6.4	1.2	21.1	16.0	12.4	12.5	38.0
70a	475 ± 1	445 ± 3	8.04	9.45	0.1	0.3	2.5	0.2	1.5	4.0	11.3	20.1	63.1
70b	475 ± 2	500 ± 5	6.96	8.10	0.2	0	4.2	0.6	1.2	3.2	10.7	18.2	66.6
70c	475 ± 2	520 ± 16	6.17	7.77	0.7	0.3	7.6	2.5	5.4	3.8	9.7	12.8	68.3
70d	476 ± 1	480 ± 9	6.16	6.72	2.5	0	10.1	5.6	5.7	5.8	6.0	6.4	76.1
70e	478 ± 2	560 ± 10	6.16	7.07	3.9	0	12.0	9.5	5.6	6.7	3.3	2.2	82.2
70f	473 ± 1	478 ± 7	6.16	7.29	4.1	0.3	12.7	10.5	7.0	9.3	0	2.5	81.2
70g	474 ± 1	403 ± 7	5.92	7.07	4.7	0.3	13.7	11.0	6.3	8.4	0	1.2	84.1
70h	475 ± 1	600 ± 13	5.33	6.40	4.2	0.3	14.0	10.0	7.9	7.1	1.8	1.2	82.7
70i	475 ± 2	466 ± 3	8.02	8.65	0.4	0	2.8	0.5	2.1	3.4	10.8	18.7	64.9
70j	477 ± 1	500 ± 3	7.53	8.70	0.7	0	4.8	1.0	3.1	3.2	10.2	16.2	67.4
70k	474 ± 2	518 ± 7	6.73	7.45	1.0	0	6.8	2.7	5.1	3.8	9.5	11.9	69.6
70l	475 ± 2	545 ± 10	6.57	7.15	2.2	0.1	9.7	5.6	6.8	4.9	4.1	6.2	78.0
70m	478 ± 1	560 ± 8	6.16	6.83	2.5	0.1	10.0	7.1	7.2	5.0	4.6	2.3	80.9
70n	477 ± 1	550 ± 5	5.61	6.26	2.7	0.1	10.0	8.0	7.4	5.6	2.7	1.7	82.6
70o	475 ± 2	482 ± 5	6.98	7.66	0	0	3.0	0.9	1.6	7.3	1.8	17.5	71.9
70p	475 ± 1	484 ± 4	6.41	7.04	0.3	0	3.4	0.8	1.7	5.5	6.2	17.6	69.0
70q	475 ± 2	496 ± 4	5.78	6.25	0.3	0.2	5.1	1.6	4.6	4.6	8.0	14.1	64.7
70r	475 ± 2	500 ± 3	5.29	5.66	0.4	0.2	6.3	2.2	4.8	5.7	7.2	12.9	69.4
70s	475 ± 2	500	4.72	5.17	0.7	0.2	7.6	3.3	4.5	5.0	5.4	6.8	78.3
70t	475 ± 1	500	4.01	4.57	0.9	0.3	9.3	7.0	4.5	6.8	1.4	3.2	82.1
70u	475	500	6.90	—	1.1	0.4	6.4	4.3	—	—	—	—	—
70v	475	500	6.03	6.61	2.4	0.3	10.7	7.9	—	3.9	5.7	3.3	—
70w	475 ± 1	500	5.78	6.34	1.2	0.2	9.7	4.8	5.8	6.6	6.3	17.0	64.3
70x	475 ± 1	500	4.78	5.47	2.0	0.6	10.9	8.4	6.0	7.1	0.4	1.7	8.3

* (C₃H₆ + H₂) * (C₂H₄ + CH₄ + H₂)

Run No.	Temperature		Time	Pressure	TOTAL PRODUCT										Composition										Moles Reacted Propane: Per 100 Product	Ratio Reacted Propane: Oxygen	MATERIAL BALANCE			
	Inlet	Outlet			CH ₄	C ₂ H ₆	C ₃ H ₈	O ₂	CH ₃ OH	CH ₃ CHO	H ₂ O ₂	H ₂ O	CO	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₈	O ₂	CH ₃ OH	CH ₃ CHO	H ₂ O ₂	H ₂ O	Output g	Input g						
97	352	300	4.9	2.0	0.2	0.28	0.3	0.1	0.1	0.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
98	375	300	4.8	18.2	2.4	0.35	0.2	0.1	0.1	0.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
99	400	300	4.9	9.5	1.4	0.35	0.2	0.1	0.1	0.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
100	425	300	4.8	5.3	1.0	0.3	0.1	0.1	0.1	0.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
101	450	300	4.9	10.2	2.4	0.1	0.1	0.1	0.1	0.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
102	475	300	4.5	49.3	20.3	3.4	0.2	11.5	8.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
103	475	300	4.9	18.4	2.4	0.28	0.3	1.2	0.1	0.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
104	475	300	5.1	25.9	4.4	0.5	0.2	2.3	0.2	0.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
105	475	300	5.7	31.2	4.4	0.86	0.3	2.4	0.2	0.6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
106	475	300	6.6	38.1	5.1	0.92	0.2	2.6	0.4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
107	475	300	8.0	42.0	5.2	1.36	0.1	3.1	0.5	0.3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
108	475	300	8.2	60.0	8.2	2.23	0.3	3.5	0.6	0.4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
109	475	300	9.3	64.7	9.3	2.6	0.4	3.7	0.7	0.8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
110	475	300	9.5	83.3	10.3	3.4	0.4	4.4	0.6	1.6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
111	475	300	11.8	94.0	11.8	4.0	0.5	5.1	0.9	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
112	475	300	12.7	11.1	3.5	0.1	0	2.4	0.2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
113	475	300	12.7	22.0	6.0	0.2	0	4.0	0.6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
114	475	300	14.1	48.6	3.3	0.6	0.3	6.7	2.3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
115	475	300	14.0	74.5	10.9	2.1	0	8.4	4.6	0.6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
116	475	300	14.0	93.4	25.8	3.1	0	9.7	7.6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
117	475	300	14.9	94.6	28.2	3.3	0.2	10.3	8.5	0.7	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
118	475	300	14.0	97.8	30.0	3.8	0.2	11.1	8.9	1.2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
119	475	300	14.5	97.3	29.3	3.4	0.2	11.5	8.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
120	475	300	14.6	23.2	3.9	0.4	0	2.6	0.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
121	475	300	14.6	39.8	6.7	0.6	0	4.5	1.0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
122	475	300	14.6	61.8	10.8	0.9	0	6.1	2.4	0.2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
123	475	300	14.0	93.4	17.4	1.9	0.1	8.3	4.8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
124	475	300	14.2	97.5	19.4	2.1	0.2	8.5	5.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
125	475	300	14.0	97.2	21.0	2.3	0.1	8.6	6.9	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
126	475	300	14.0	25.5	4.3	0	0	2.7	0.9	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
127	475	300	14.6	30.9	4.7	0.3	0	3.3	0.8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
128	475	300	14.8	48.2	7.4	0.3	0.2	4.8	1.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
129	475	300	14.2	62.0	9.3	0.4	0.2	5.8	2.0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
130	475	300	14.9	79.7	12.2	0.7	0.2	6.8	3.0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
131	475	300	14.0	94.5	17.9	0.8	0.3	8.4	6.3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
132	475	300	14.8	94.0	13.0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
133	475	300	14.6	97.3	21.4	1.4	0.3	8.9	5.6	0.3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
134	475	300	14.6	86.0	14.1	1.0	0.2	9.0	4.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
135	475	300	14.6	97.8	22.0	1.7	0.5	9.1	5.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
136	475	300	14.6	97.8	22.0	1.7	0.5	9.1	5.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

$\cdot (C_2H_6 + H_2)$

$\cdot (C_2H_4 + CH_4)$

$\cdot (C_2H_4 + CH_4 + H_2)$

$$\cdot (C_2H_4 + H_2) \quad \cdot (C_2H_4 + C_2H_6)$$

$$\cdot (C_2H_4 + C_2H_6)$$

$$\cdot (C_2H_4 + H_2)$$

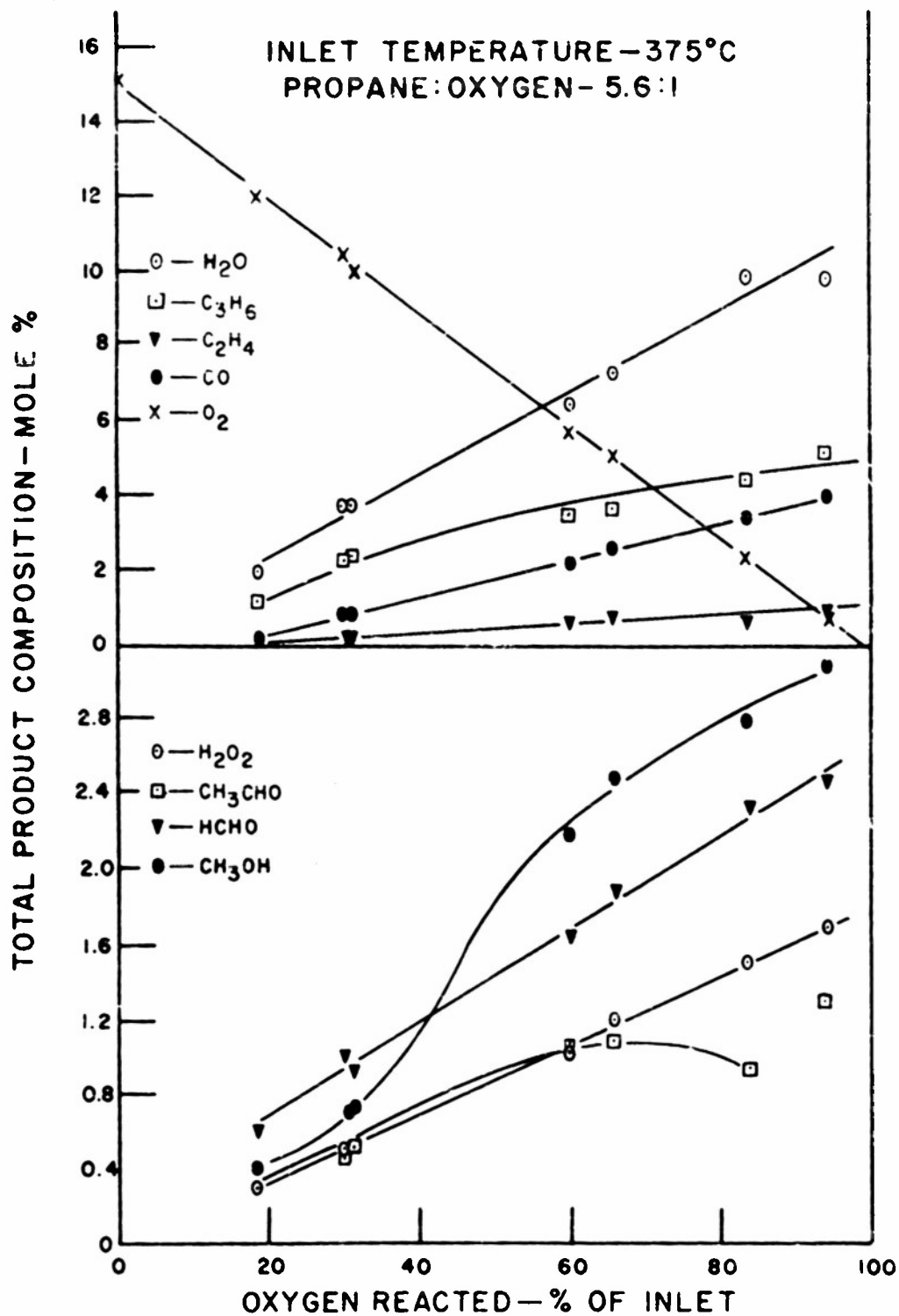


FIGURE 2
PRODUCTS OF PROPANE OXIDATION

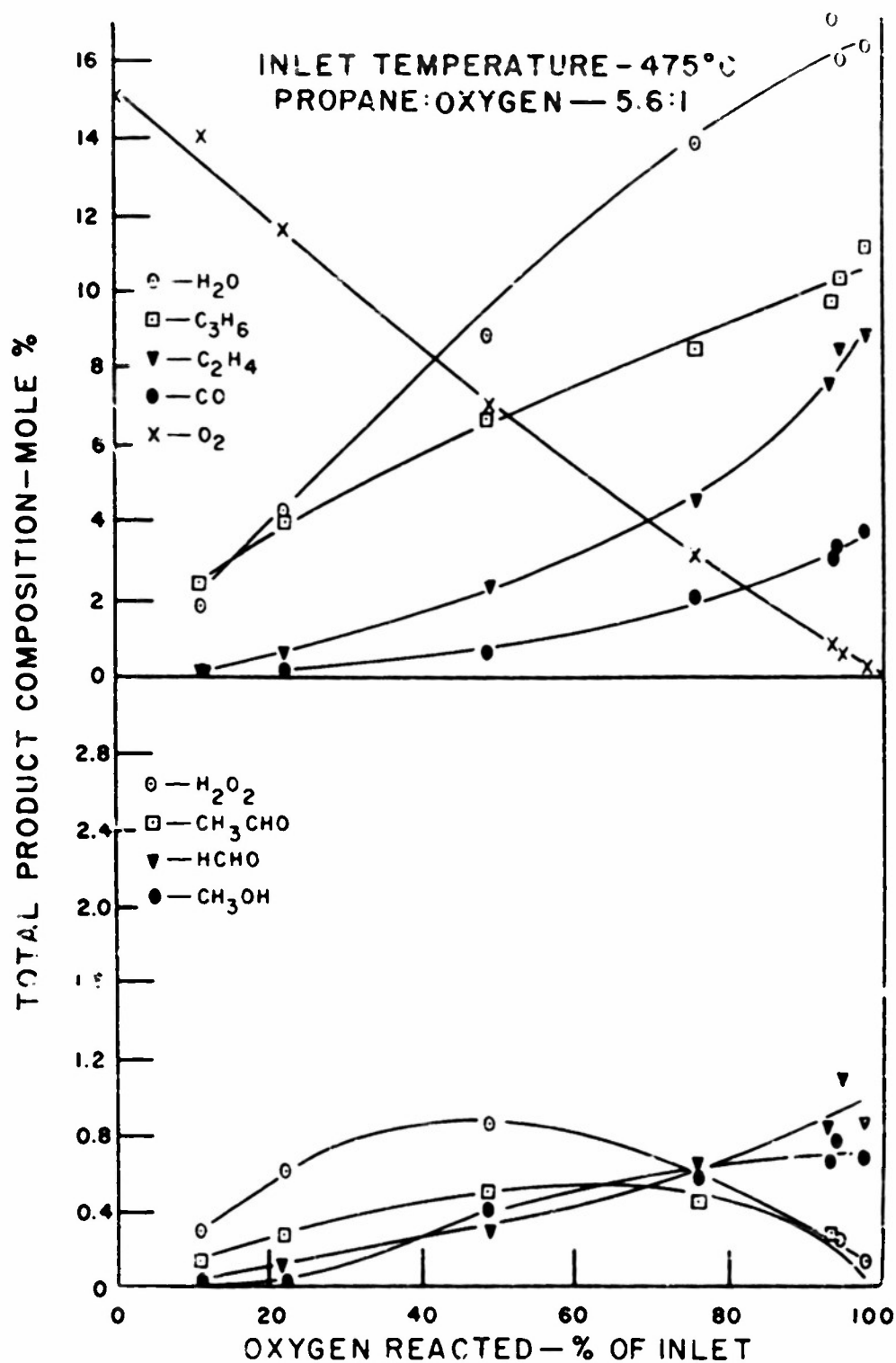


FIGURE 3
PRODUCTS OF PROPANE OXIDATION

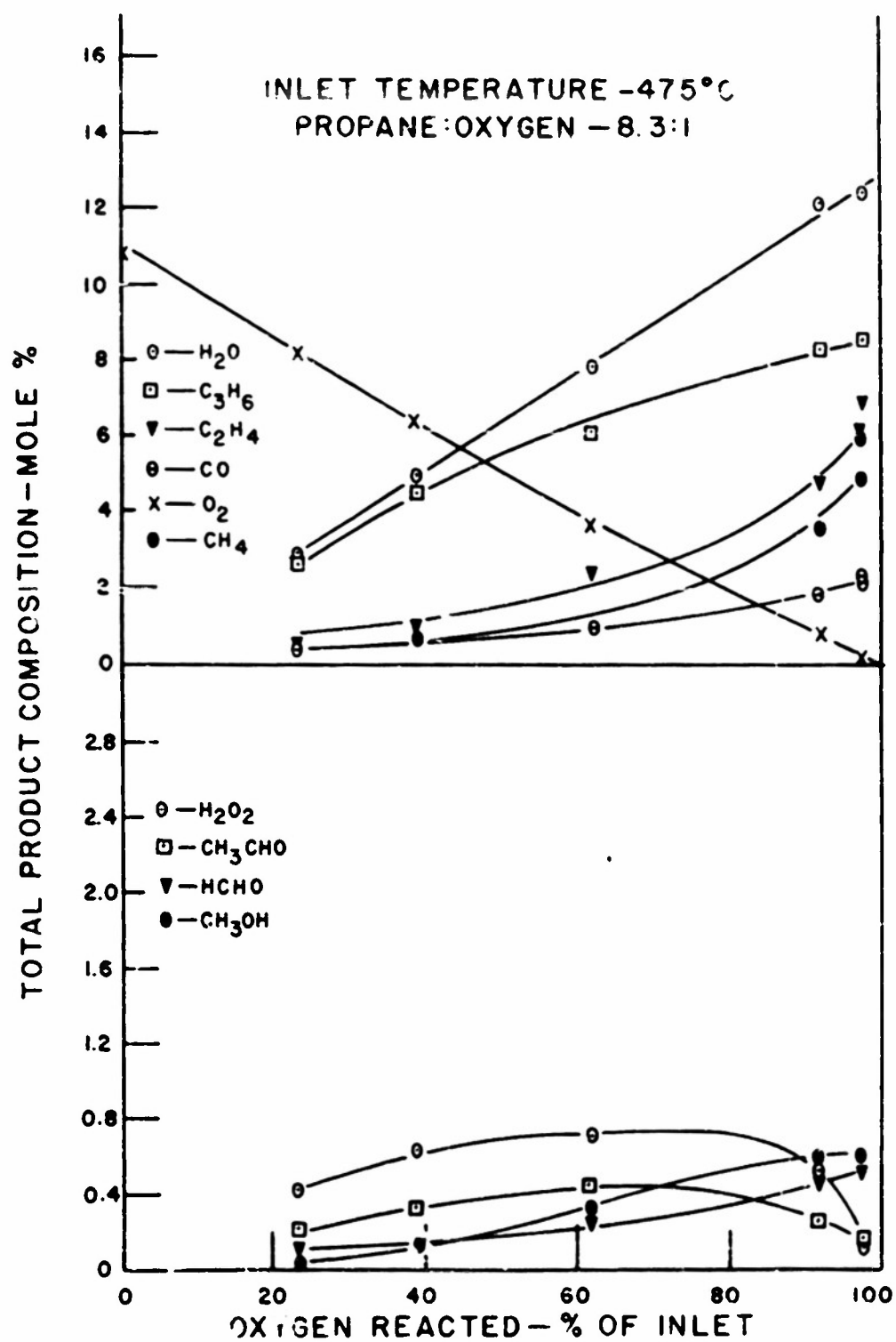


FIGURE 4
PRODUCTS OF PROPANE OXIDATION

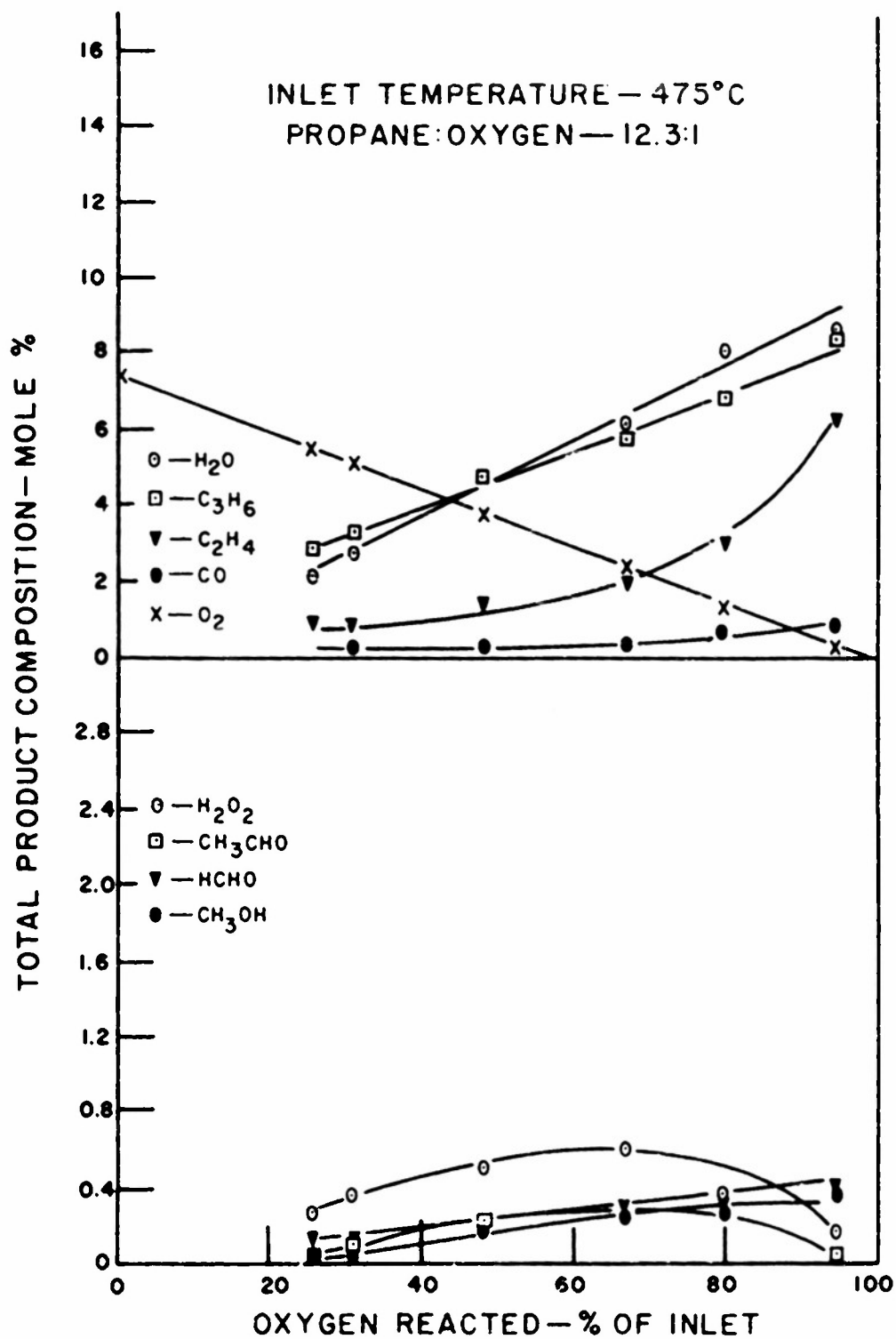


FIGURE 5
PRODUCTS OF PROPANE OXIDATION

as the "propane concentration" in the exhaust gas were obtained by difference and, as described above, may include not only propane but small amounts of hydrogen, and/or methane as well, depending upon the run.

The data given in Table II were employed in the calculation of the total product composition presented in Table III. These data represent the total gas stream composition before condensation, assuming no reaction occurred in the condenser.

The significance of the results is best seen by plotting the product composition as a function of the percent of the inlet oxygen reacted, for each of four different inlet conditions studied. This has been done in Figures 2 to 5. The concentrations of propane, hydrogen, carbon dioxide, and methane have been omitted from the figures. The method of plotting used in the figures gives a better correlation of the data than a plot using residence time as the abscissa since, as is characteristic of chain reactions, slight changes in flow rate or temperature may cause a pronounced change in the extent of reaction observed. As a specific example of the time scale involved, at 475°C. and a propane:oxygen mole ratio of 5.6, the apparent induction period was about 3 seconds: at 3.7 seconds, 22% of the inlet oxygen had reacted; at 4.0 seconds, 97% of the oxygen had reacted.

The two products formed in greatest quantities were water and propylene; however, at the higher reaction temperature,

considerably more ethylene, propylene, and water were formed, but less oxygenated products. These results can be observed in Figures 2 and 3 which compare inlet temperatures of 375° and 475°C respectively. It should be noted that as reaction progresses at 475°C the concentrations of hydrogen peroxide and acetaldehyde pass through a maximum value, while all other product concentrations increase continuously. The effects of a change in inlet oxygen concentration at 475°C are shown in Figures 3, 4, and 5. A decrease in oxygen concentration decreased the reaction rate and also caused a proportionate decrease in the concentrations of the oxygenated organic products.

The existence of a negative temperature coefficient for the reaction rate was investigated using a 5.6:1 ratio of propane: oxygen. As the inlet gas temperature was increased from 350°C, the amount of oxygen reacting in 4.8 to 4.9 seconds increased from 2% at 350° to a maximum of 18% at 375°C, declined to a minimum of 5% at 425°, and then increased to 10% at 450° and to 97% at 475°. These results are very similar to those of Kooijman (13), who reported a negative temperature coefficient for a 9:1 mixture in the range of 375° to 430°C.

All of the data presented in this report were obtained with all of the exit gas leaving at the top of the reactor, as shown in Figure 1.

Since the reaction time was varied by varying the flow rates of the inlet gases, this raises the question of whether the observed results were due in part to changes in the mixing characteristics of the mixer at the bottom of the reactor. To answer this question, preliminary studies were conducted in which a portion of the gas was withdrawn through one of the gas sample ports. By this means the residence time could be changed without changing the inlet flow rates. A comparison of the data for runs at the same residence time but with linear flow rates differing by nearly 100%, indicated a slightly increased amount of reaction at the higher flow rates, which was probably due to the change in heat transfer characteristics. There were no changes in product composition other than those caused by differences in the extent of reaction, thus indicating that the rate of mixing was not a limiting factor on the reaction as studied here.

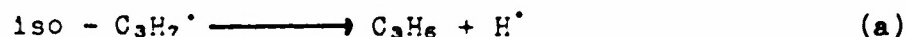
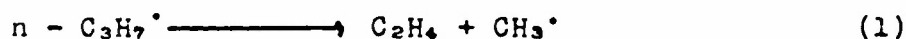
Discussion

Some insight into the reaction mechanism involved here may be obtained by a consideration of first, the quantitative yields of the various products, second, the effects of oxygen concentration and reaction temperature upon the yields of the various products, and third, the heats of reaction and the energies of activation of the various possible reaction steps which could account for the results observed. The reaction is

free radical in nature, presumably proceeding through the propyl free radical. The free radical nature of the reaction is evidenced by such characteristics as the apparent induction period. In the discussion below, the important reactions have been given arabic numbers and are summarized in Table V. Those reactions considered of minor importance in the over-all mechanism here are designated by a lower-case letter.

Formation of the Olefins

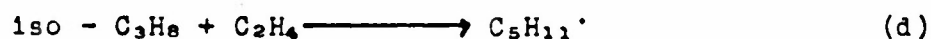
Chernyak and Shtern (2) propose that the olefins are formed by the thermal decomposition of the propyl free radical, the n-propyl forming ethylene and the iso-propyl forming propylene.



The occurrence of reaction (1) here is evidenced by the appreciable yield of methane that was obtained in this investigation and is also demonstrated directly by the work of Paneth and Lautsch (20) who decomposed tetra-n-propyl lead at about 400°C. They attempted to identify the products of the decomposition by means of lead, zinc, and antimony mirrors; the only identifiable organo metallic compounds were methyl compounds. They therefore concluded that any propyl radicals formed decomposed rapidly by means of reaction (1).

The reactions of the iso-propyl radical are not as clearly defined as those of the n-propyl radical. The topic has been reviewed by Steacie (29), who concluded that the iso-propyl is somewhat more stable than the n-propyl radical and that reaction

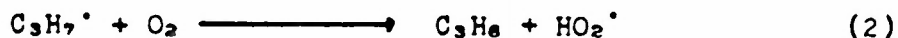
(a), due to its endothermicy, would not be important. The conclusion that secondary alkyl radicals are more stable than primary is supported by reports concerning the behavior of the butyl free radical (25). Di-n-butyl mercury and di-sec. butyl mercury were decomposed by passing the vapors at about 3 mm. pressure through a Pyrex tube heated to 490°C. Three-quarters of the n-butyl radicals decomposed into ethylene and the ethyl free radical, a reaction equivalent to reaction (1). The sec-butyl radical was more stable and reacted 77% by combination and disproportionation reactions similar to reactions (b) and (c), listed below. The fact that the yield of hydrogen in the present investigation was only a small fraction, approximately one-tenth, of the propylene yields indicates that reaction (a) is of no importance in the present case. There is considerable evidence that the iso-propyl radical enters into combination, disproportionation, and addition reactions (29).



The literature reports indicate, however, that the formation of propylene by reaction (c) is accompanied by the formation of hexane by reaction (b). The fact that in this present work no 2,3 - dimethyl butane was found among the products of oxidation at 475°C indicates that reaction (c) is not the source of the propylene. The infrared analysis also detected,

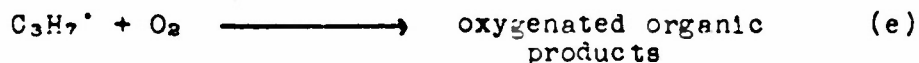
at most, only traces of pentanes, thus enabling one to neglect reactions of the type (d). The work of Rice and Evering (24) suggests that the iso-propyl radical decomposes at 450° to 550°C to form ethylene and methyl radicals, and thus reaction (1) may not be limited solely to the n-propyl radical.

Since water is the major product of the reaction, it is logical to seek a connection between its formation and that of propylene. There is no simple reaction that will directly relate the two products. It is important to note also that hydrogen peroxide has been reported as a major product at times when large quantities of olefins were produced. For example, Lacomble (15) reported a hydrogen peroxide yield of 0.52 moles per mole of propane reacted, employing a reaction temperature of 470°C, a propane:oxygen ratio of 9:1 and a residence time of 5 seconds. Cook (3) reported a maximum hydrogen peroxide yield of 0.30 moles per mole of propane reacted, when using a 5.7:1 ratio of propane:oxygen at 527°C. The first step in the formation of hydrogen peroxide, a reaction of the propyl radical with oxygen, was suggested tentatively by Lewis and Von Elbe (17) for the ethane - oxygen reaction.



The reaction is approximately thermo-neutral; it is 18 kcal exothermic if the calculation is based on the HO_2^\cdot dissociation energy reported by Walsh (30) and 6 kcal endothermic if based

on the dissociation energy reported by Evans, Hush, and Uri (5). The propyl radical and oxygen also react by an alternate path to form oxygenated organic products.



This reaction will be discussed in greater detail below.

The set of reactions, (2) and (e), predicts that the fraction of the propyl radicals reacting with oxygen which form propylene should be a function of the temperature only. This assumes that the relative rates of reactions (2) and (e) are determined by the individual energies of activation. This fraction was calculated from the data in the following manner: first, the number of moles of propyl free radicals reacting by (2) was assumed equal to the propylene formed; second, the total number of moles of propyl radicals reacting with oxygen (the sum of reactions (2) and (e)) was calculated to be the total moles of propane reacted minus the moles of ethylene formed. The ethylene is subtracted from the total because it is believed to be the only product formed from the propyl radical which does not involve reaction with oxygen. The results of the calculation are presented in Figure 6 in which the ordinate represents the moles of propylene formed per mole of propyl radical reacting with oxygen. It is seen that this fraction is independent of the inlet oxygen concentration and of the extent of the reaction, but varies with the temperature. This is exactly as predicted

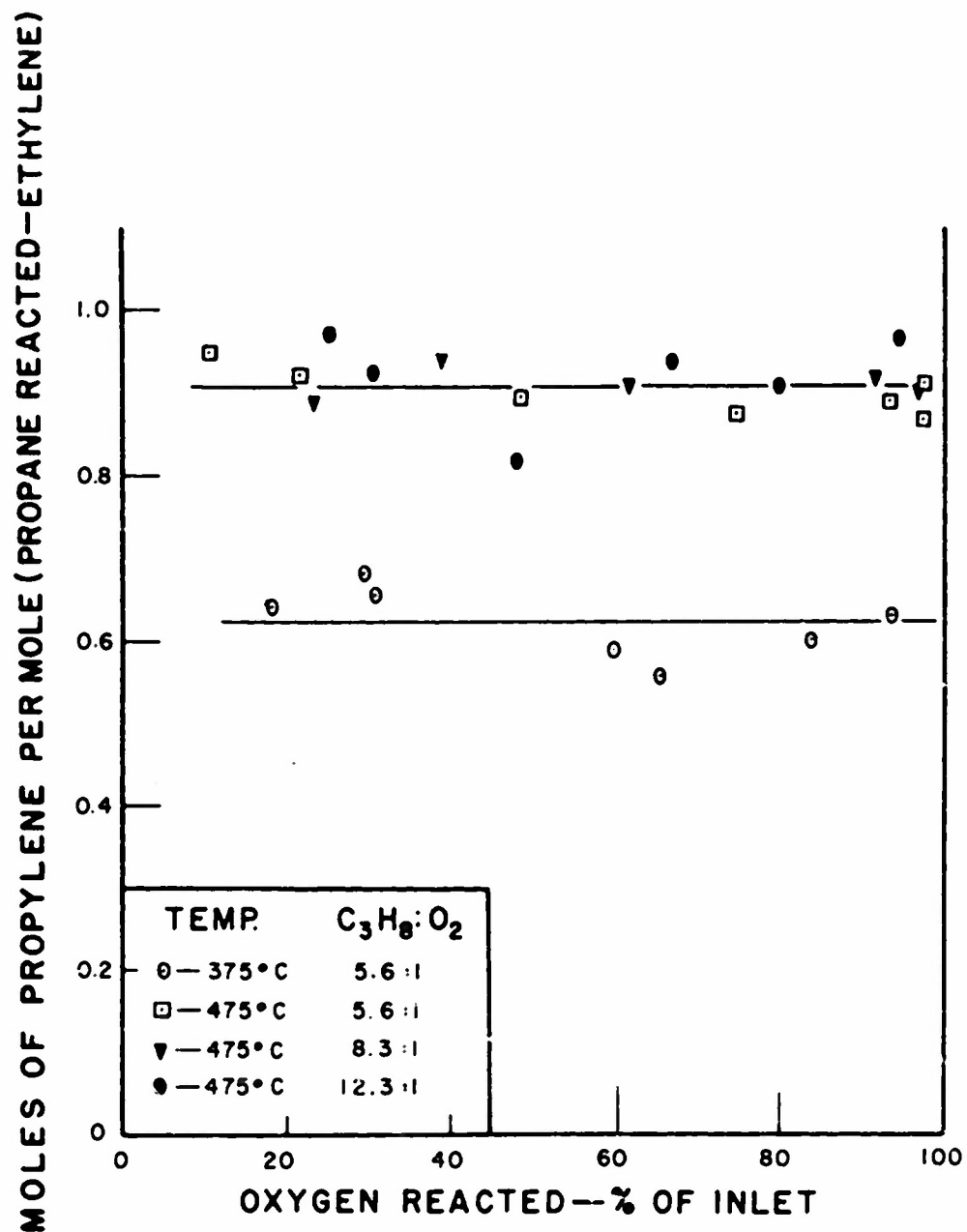


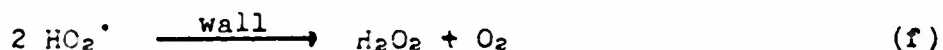
FIGURE 6

TEST OF POSTULATED MECHANISM
REPRESENTED BY EQUATIONS 2 AND e

by the set of reactions, (2) and (e).

The formation of hydrogen peroxide and water

Hydrogen peroxide can be formed from two hydroxyl radicals only by a wall reaction at very low temperatures (26). The logical source for hydrogen peroxide is the peroxy free radical formed in reactions (1) and (2). The radical has been considered relatively unreactive (17), and it therefore may be thought that the formation of hydrogen peroxide takes place at the wall.



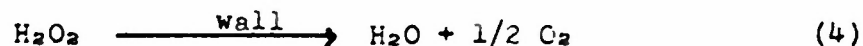
This reaction however must be discarded in favor of a gas phase reaction after a consideration of the experimental results of other workers. For example, Gelb and Harteck (7) found that under conditions where atomic hydrogen alone does not react with hydrocarbons, atomic hydrogen plus oxygen will give a rapid reaction, suggesting a reaction of the following type.



Additional evidence for the gas phase reaction, (3), is given by the work of Lacomble (15), who conducted the oxidation of propane in a spherical shell, introducing the reactants tangentially at the outer circumference and withdrawing the products from the center. Under these conditions of essentially homogeneous gas phase reaction, he recovered a relatively high yield of hydrogen peroxide. Jost (12) concluded that the

perhydroxy radical will react with hydrogen and hydrocarbons at reasonably low temperatures. In light of the above discussion the present authors conclude that hydrogen peroxide is formed during the reaction by means of reaction (3).

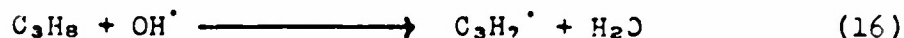
If all perhydroxyl disappeared by reaction (3) and if the hydrogen peroxide were stable and did not react further, its production would equal that of the propylene. The fact that the maximum yield actually obtained in this work was 0.25 moles of hydrogen peroxide per mole of propylene is probably due to rapid disappearance of hydrogen peroxide after being formed, as shown by the shape of the curves in Figures 3,4, and 5. There are two paths by which hydrogen peroxide may disappear; first, it may decompose at the wall, or second, it may react in the gas phase with the other organic compounds present. There is no direct evidence for or against the latter reaction, but it should be noted that hydrogen peroxide will react with aldehydes in the liquid phase (4), (14). There is, however, considerable evidence that hydrogen peroxide decomposes heterogeneously in the gas phase.



For example, when Harris (9) passed hydrogen peroxide vapors through a potassium chloride-coated tube, the hydrogen peroxide was completely destroyed. When using a clean Pyrex tube, a large fraction of the peroxide passed through undecomposed. In a reaction tube coated with potassium chloride, Pease and

Munro (23) failed to recover peroxides from propane oxidation, but did recover peroxides when using a clean Pyrex tube. Kooijman (13) reported that washing the reactor tube with hydrofluoric acid increased the yield of hydrogen peroxide from propane oxidation. Cook (3) reported that a coating of boric acid or a borate salt increased the yield. It was observed during the present work that higher yields were obtained when the reactor was new than when it had been in use for some time. The reactor surface undoubtedly plays an important role in the disappearance of hydrogen peroxide.

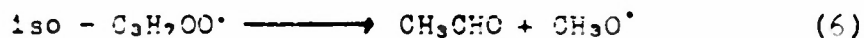
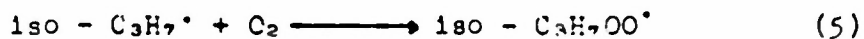
Water is also formed by the reaction of the hydroxyl radical with propane, or another hydrocarbon, to form water and a free radical.



The reaction is exothermic by 32 kcal/mole and has an activation energy estimated by McDonald and Schalla (18) to be 2 to 5 kcal.

Formation of the oxygenated organic products

The exact nature of reaction (e), which forms the oxygenated organic products, will now be discussed in greater detail. Lewis and Von Elbe (17) have reviewed the information available in the literature and propose that the isopropyl radical reacts as follows:



5



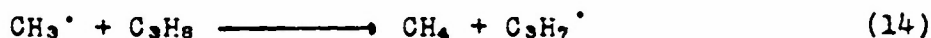
The fact that Pease and Munro (22) did not detect propionaldehyde as a product of propane oxidation is accounted for by the postulated reactions of the n-propyl radical.



The shape of the concentration curves for acetaldehyde indicates that it enters into further reactions, a conclusion supported by the work of Chernyak and Shtern (2), who added acetaldehyde as a diluent and found that its final concentration was not increased. The decomposition of acetaldehyde at 400°C is almost entirely a free radical reaction (6).



In the presence of oxygen and propane the methyl radical would participate in two competing reactions.



Steacie (29) has reported activation energies of 1.5 kcal for reaction (15) and 6 to 8 kcal for reaction (14). Due to the lower activation energy of reaction (15) one would expect a considerable fraction of the methyl radicals, formed by both reactions (1) and (13), to be oxidized to formaldehyde, even in a fuel-rich system.

Pure formaldehyde in the vapor state is more stable than acetaldehyde, but in the presence of free radicals its decomposition and oxidation must be considered. The results of the present work cannot add to the excellent discussion of Lewis and Von Elbe (17). It is important to note that the small quantity of hydrogen may have been formed by the decomposition of the formyl radical.



The calculations of Lewis & Von Elbe indicate that (18) is endothermic by 25 kcal. The decomposition is quite possible at temperatures over 400°C in systems having a deficiency of oxygen.

The theoretical yield of water and hydrogen peroxide

The validity of the postulated mechanism can be further tested by calculating the yield of water and hydrogen peroxide

which would be expected in terms of the quantities of the other products which were actually found. In developing the desired expression the water or peroxide that is formed by the chain initiating reaction, (1), is neglected, and it is assumed first, that all hydroxyl radicals react to form water, second, that all perhydroxy radicals react to form hydrogen peroxide by reaction (3), and third, that the decomposition of hydrogen peroxide proceeds entirely by reaction (4). Those reactions which form hydroxyl radicals or water directly are reaction (10), which forms an equivalent amount of ethane, reaction (8), which forms one hydroxyl radical and one water molecule, and reaction (15), which forms an equivalent amount of formaldehyde. The set of reactions (2), (3), and (4), forms a quantity of water and hydrogen peroxide equal to the propylene formed. By summing all of these reactions the following expression is derived for the total water plus hydrogen peroxide:

$$N_{H_2O} + N_{H_2O_2} = N_{C_3H_8} + N_{C_2H_6} + 2N_{(reaction(8))} + N_{total\ HCHO}$$

The set of reactions, (6), (7), and (8), specifies that the number of moles reacting by (8) will be equal to the total acetaldehyde formed minus the methanol formed.

$$N_{(reaction\ (8))} = N_{CH_3CHO\ found} + N_{CH_3CHO\ reacted} - N_{CH_3OH}$$

A carbon monoxide balance on reactions (8), (11), (13), and (18) results in the following expression:

$$N_{(\text{reaction (8)})} = N_{\text{total CO}} - N_{\text{H}_2} - N_{\text{CH}_3\text{CHO reacted}} - N_{\text{C}_2\text{H}_6}$$

Eliminating the unknown quantity, $N_{\text{CH}_3\text{CHO reacted}}$, results in the following expression for the number of moles reacting by reaction (7):

$$N_{(\text{reaction (8)})} = 1/2 \left[N_{\text{CH}_3\text{CHO found}} + N_{\text{total CO}} - N_{\text{H}_2} - N_{\text{C}_2\text{H}_6} \right]$$

Since the formaldehyde has been considered to react only by reactions (17) and (18), the total amount of formaldehyde formed can be expressed as the sum of the formaldehyde found plus the hydrogen found. The total carbon monoxide is represented by the sum of CO and CO_2 . Substituting into the original expression for total water and hydrogen peroxide results in the final expression containing only quantities which were determined by analysis of the products.

$$N_{\text{H}_2\text{O}} + N_{\text{H}_2\text{O}_2} = N_{\text{C}_3\text{H}_8} + N_{\text{HCHO}} + N_{\text{CH}_3\text{CHO}} + N_{\text{CO}} + N_{\text{CO}_2} - N_{\text{CH}_3\text{OH}}$$

The results of the calculation are presented in Table IV in which the water calculated to be formed from the oxygenated organics alone is also listed for comparison with the total

Table IV

Test of Postulated Mechanism from Observed Yields
of Water Plus Hydrogen Peroxide

Run No.	Inlet Temp. °C	% Inlet Oxygen Reacted	Calc'd H ₂ O* from reactions (8), (10), (15)	H ₂ O found* by analysis	Total Calc'd H ₂ O + H ₂ O ₂ *	H ₂ O + H ₂ O ₂ found* by analysis
88	375	18.4	1.1	2.0	2.3	2.3
90	"	29.9	1.8	3.8	4.1	4.3
91	"	31.2	1.9	3.7	4.3	4.2
92	"	34.1	2.0	4.1	4.6	4.8
93	"	42.0	2.3	5.3	5.4	6.2
96	"	60.0	3.0	6.5	6.5	7.5
97	"	65.7	3.5	7.3	7.2	8.5
95	"	83.3	4.3	9.8	8.7	11.3
94	"	94.0	5.2	9.8	10.3	11.5
78a	475	11.1	0.3	1.8	2.7	2.1
78b	"	22.0	0.6	4.2	4.6	4.8
79a	"	48.6	1.3	8.8	8.0	9.7
81a	"	75.5	2.6	13.8	11.0	14.4
81b	"	93.5	3.6	17.1	13.3	17.4
80b	"	94.6	3.8	16.1	14.1	16.4
80a	"	97.8	4.2	16.4	15.3	16.5
79b	"	97.3	3.9	16.4	15.4	16.5
82a	"	23.2	0.6	2.8	3.2	3.2
83a	"	38.8	0.9	5.0	5.4	5.6
82b	"	61.8	1.3	7.8	7.4	8.5
84a	"	91.8	2.1	12.1	10.4	12.6
83b	"	97.5	2.3	12.4	10.8	12.6
84b	"	97.2	2.4	12.5	11.0	12.6

76a	475	25.5	0.1	2.2	3.1	2.5
77a	"	30.9	0.5	2.7	3.8	3.1
75a	"	48.2	0.7	4.8	5.5	5.3
77b	"	67.0	0.9	6.2	6.7	6.8
75a	"	79.7	1.2	8.1	8.0	8.5
76b	"	94.5	1.2	8.5	9.6	8.7
73	"	86.0	1.7	10.0	10.0	11.4
74	"	93.8	2.4	12.6	11.7	12.7

*moles per 100 moles of total product

amount of water which was actually formed. The most significant fact is that the formation and oxidation of the aldehydes accounts for no more than fifty percent of the water actually formed. This is a strong indication that a reaction, such as (2), connecting water and olefin production is very necessary. The calculated values of water plus hydrogen peroxide in Table IV are often slightly higher at the early stages of reaction and slightly lower at the later stages than the values actually found. This trend is easily accounted for by the fact that first, some of the water passes through the condenser as vapor and second, the chain initiating step, (1), has been neglected in the calculation. There is also the possibility that a small fraction of the hydrogen peroxide decomposed in the gas phase by splitting into two hydroxyl radicals, a reaction possessing an activation energy of approximately 45 kcal (16).

The negative temperature coefficient

The negative temperature coefficient of the reaction rate is an important phenomenon which must be explained by the oxidation mechanism. In the region from 375° to 425°C the rate was found to decrease with increasing temperature. Judging from the changes in product composition in Figures 2 and 3, the shift in reaction which occurs with increasing temperature is an increase in reaction (2) and a decrease in reactions (5) and (9). A decrease in the over-all reaction rate

would occur if the products of reaction (2), propylene and perhydroxy radicals, were less active in continuing the chain than the products of reactions (5) and (9), which are aldehydes, methoxy radicals, and hydroxy radicals. Propylene is known to inhibit free radical reactions (11), while aldehydes participate readily. The perhydroxy radical is considered to be less reactive than the hydroxy radical (17). It therefore appears that the decrease in the over-all rate of reaction was caused by the increased production of propylene with increasing temperature.

Industrial aspects of the reaction

Although appreciable yields of useful chemical products are obtained, it is very difficult at the present time to evaluate the industrial possibilities of the process. Several very important questions remain to be answered. The manner in which the reactor surface influences the reaction is not fully understood. It is known, however, that the yield of hydrogen peroxide varies greatly depending on the amount and kind of surface present and would probably be higher for reactors of lower surface-volume ratios and constructed with more inert surfaces. The effects of adding end products to the feed stream, such as would occur on recycling, have not been fully investigated. Reports indicate that dilution of the feed stream with olefins has adverse effects (3,15), indicating the necessity

for considerable treatment of the recycle gas. The separation of the condensate into marketable chemicals presents a difficult problem that requires further clarification. A study of this separation problem is reported elsewhere (28).

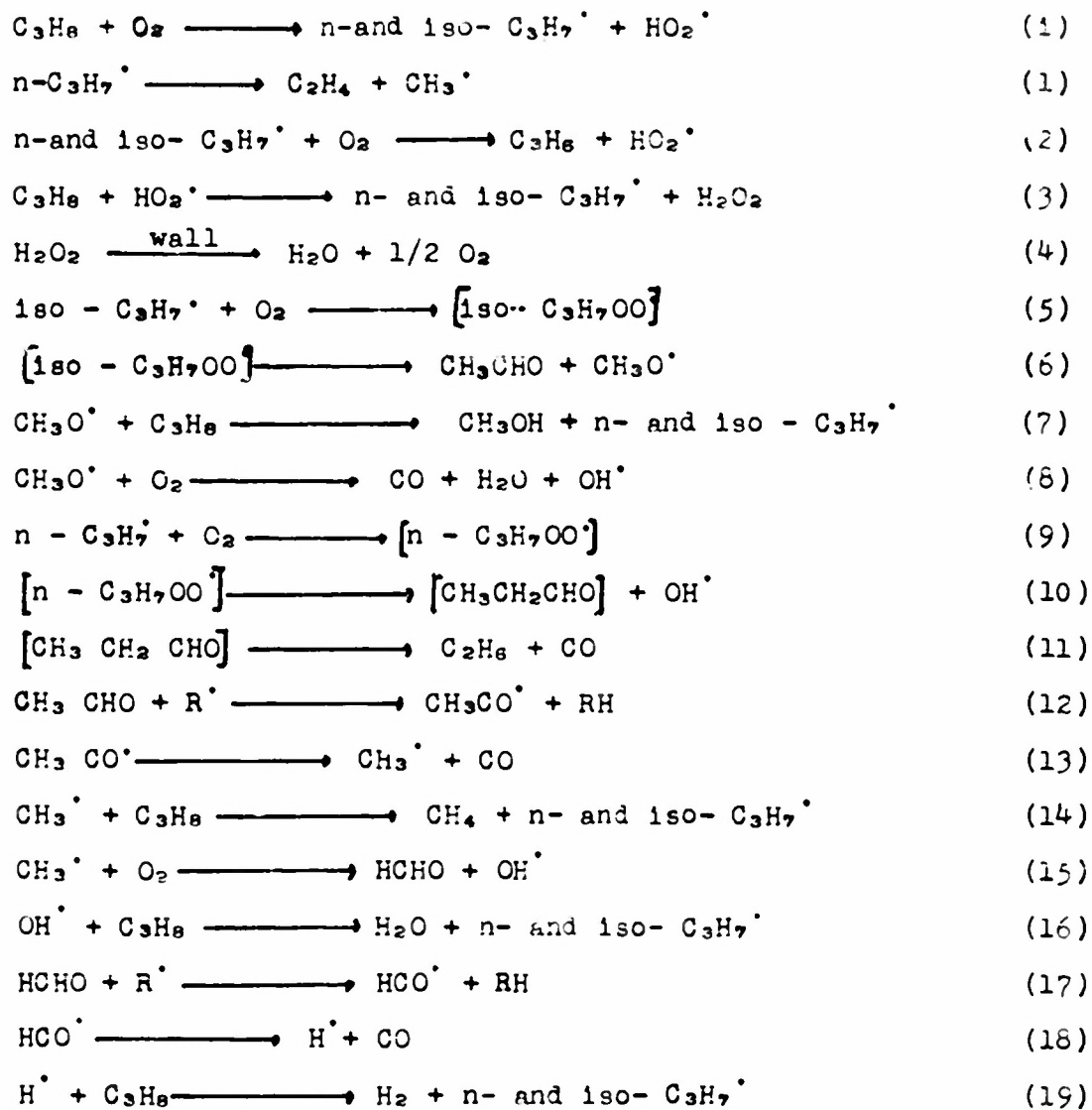
The highest yield of hydrogen peroxide obtained here was 0.195 mole per mole of oxygen reacted or 0.12 mole per mole of propane reacted. This occurred at 475°C and with a propane: oxygen mole ratio of 5.6. This yield could undoubtedly be substantially increased, as discussed above.

Conclusions

The reactions which are considered of importance here are summarized in Table V. Under the conditions of this work the results indicate that a key reaction occurs between the propyl radical and oxygen, which may follow two alternate paths, one forming oxygenated organic products and the other forming propylene and the perhydroxy radical. The perhydroxy radical reacted with propane, or another hydrocarbon, to form hydrogen peroxide and a free radical. The disappearance of hydrogen peroxide during the reaction is attributed to a wall decomposition forming water and oxygen. The reactions which form the oxygenated organic products are adequately interpreted by the reaction mechanism proposed by Lewis and Von Elbe (17). The oxidation of the aldehydes also is accounted for by their mechanism, but the results of this work did not give conclusive evidence in this respect. The reactions which form the oxygenated

Table V

Reactions of Significance in the Partial
Oxidation of Propane



organic products are inadequate to account for the quantities of water and hydrogen peroxide which are formed. It is necessary to include in the reaction mechanism a reaction, such as (2), which will connect the olefin production with that of water. The negative temperature coefficient of the reaction rate can be explained on the basis of the two alternate reactions of the propyl radical with oxygen. With an increase in temperature, the reaction forming propylene increases relative to that forming oxygenated organics, and since the products of the first reaction are less reactive, this results in a decrease in the over-all rate in the region 375° to 475°C.

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